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(U) COLLABORATIVE EXPERIMENTAL AND THEORETICAL STUDY OF THE PHOTODISSOCIATION AND REACTIONS OF THE AZIDE RADICAL

12. PERSONAL AUTHOR(S)
Paul J. Dagdigian and Millard H. Alexander

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A theoretical investigation of the energetics of the dissociation of ground state hydrazoic acid HN_3 and the azide radical N_3 has been carried out through complete active space SCF and multireference configuration interaction calculations with large basis sets. Of particular interest was (a) the determination of the bond dissociation energies of HN_3 and N_3, (b) the location of the geometry and topology of the transition state for spin-forbidden decomposition and the corresponding activation energy, and (c) the investigation of the magnitude and origin of exit channel barriers in the spin-allowed decomposition

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pathway. Preliminary results have also been obtained in three related experimental studies involving the determination of the internal state distributions of (a) the $NH(a^1\Delta)$ product from the $H + N_3$ reaction, (b) the N_2 photofragment from the uv photodissociation of HN_3, and (b) the $NH(X^3\Sigma^-)$ product from the electronic quenching of $NH(a^1\Delta)$ by N_2.
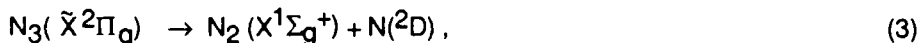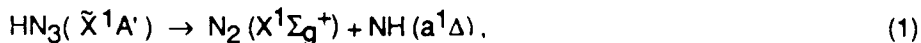
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COLLABORATIVE EXPERIMENTAL AND THEORETICAL STUDY

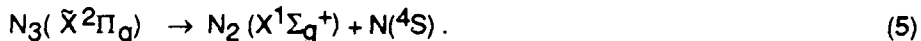OF THE PHOTODISSOCIATION AND REACTIONS OF THE AZIDE RADICAL

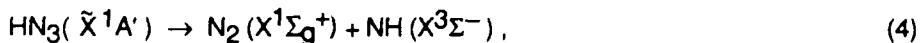Paul J. Dagdigian and Millard H. Alexander

Alexander has been involved in a theoretical investigation of the energetics of the dissociation of ground state hydrazoic acid HN_3 and the azide radical N_3. This includes the spin-allowed decomposition pathways on the lowest potential energy surface,

$$HN_3(\tilde{X}^1A') \rightarrow N_2(X^1\Sigma_g^+) + NH(a^1\Delta), \tag{1}$$

$$\rightarrow N_3(\tilde{X}^2\Pi_g) + H(^2S), \tag{2}$$

$$N_3(\tilde{X}^2\Pi_g) \rightarrow N_2(X^1\Sigma_g^+) + N(^2D), \tag{3}$$

as well as the spin-forbidden channels,

$$HN_3(\tilde{X}^1A') \rightarrow N_2(X^1\Sigma_g^+) + NH(X^3\Sigma^-), \tag{4}$$

$$N_3(\tilde{X}^2\Pi_g) \rightarrow N_2(X^1\Sigma_g^+) + N(^4S). \tag{5}$$

Complete active space SCF and multireference configuration interaction calculations with large basis sets have been used (a) to determine the bond dissociation energies of HN_3 and N_3, (b) to locate the geometry and topology of the transition state for spin-forbidden decomposition and the corresponding activation energy, and (c) to investigate the magnitude and origin of exit channel barriers in the spin-allowed decomposition channel. The barrier to the spin-forbidden decomposition of HN_3 [Eq. (4)], including zero-point corrections, is predicted to be $E_a = 16,152$ cm^{-1}, which is in good agreement with the HN_3 decomposition lifetimes seen in the overtone pumping experiments of King, Stephenson, Casassa, and Foy at NIST, which indicate that E_a lies between 15,000 cm^{-1} and 17,700 cm^{-1}. The topology of the potential energy surface of HN_3 in the region of the singlet-triplet crossing has also been investigated.

In the spin-allowed (singlet) decomposition channel [Eq. (1)] our calculations indicate the existence of

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a small barrier of height 1000 – 1500 cm^{-1}. This barrier can be attributed to orbital constriction: As the N_2–NH distance decreases, Pauli repulsion with the lone-pair σ orbital on the N_2 forces one of the NH π orbitals out of the occupied space. This calculated barrier is consistent with the observation by the group at NIST of a hyperthermal ($E_{tr} \approx 1700$ cm^{-1}) translational energy of the nascent NH($a^1\Delta$) products in the IRMPD decomposition of HN_3. Also, a small barrier is consistent with the small rate constant observed by Stuhl and coworkers for quenching of NH($a^1\Delta$) by N_2. In the absence of a barrier, quenching should be efficient, mediated by approach on the singlet surface followed by crossing to the triplet surface, as proposed some time ago by Fisher and Bauer as the quenching mechanism in the isoelectronic $O(^1D)+N_2$ system.

The barrier for the spin-forbidden decomposition of N_3 [Eq. (5)] is calculated be 212–215 kJ/mol, slightly higher than the comparable barrier in HN_3. The N–NN bond dissociation energy in N_3 is predicted to be 3–12 kJ/mol, much less than the experimental estimate of 53.9 ± 20.9 kJ/mol obtained using the JANAF value of the heat of formation of N_3 (417.0 ± 20.9 kJ/mol). However, our estimate of the N–NN bond dissociation energy is consistent with the value of 2.2± 20.9 kJ/mol which is obtained with the larger heat of formation of N_3 (468.6 ± 20.9 kJ/mol) advocated by Brauman and coworkers. As in the case of HN_3, there also exists a slight barrier in the exit channel for the spin-allowed decomposition of N_3 leading to $N(^2D)$ products [Eq. (3)].

In Dagdigian's laboratory, three different types of experiments which probe the dynamics of processes involving potential energy surfaces of HN_3 have been set up, and preliminary results have been obtained. These studies involve the determination of the internal state distribution of the products of various collisional processes, namely (1) the NH product from the H + N_3 chemical reaction, (2) the N_2 photofragment from the uv photodissociation of HN_3, and (3) the NH($X^3\Sigma^-$) product from the electronic quenching of NH($a^1\Delta$) by N_2.

In our crossed beam study of the H + N_3 reaction,

$$H + N_3(\ \tilde{X}^2\Pi_g)\ \rightarrow\ NH(X^3\Sigma^-, a^1\Delta) + N_2\ (X^1\Sigma_g^+)\ , \tag{6}$$
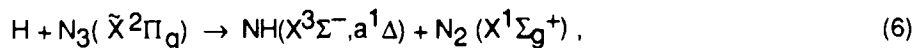
hydrogen atoms are prepared in a supersonic microwave discharge source. Azide radicals are prepared by the reaction of fluorine atoms, produced in a CF_4/Ar microwave discharged flow, with hydrazoic acid.

We found that our previously employed source of azide radicals, namely the thermal decomposition of lead azide, was not sufficiently intense, stable, or long-lived to be suitable for these studies. We have thus far observed the $v=0$ and 1 vibrational levels of $NH(a^1\Delta)$ product through laser fluorescence excitation excitation of the NH c – a (0,0) and (0,1) bands. The rotational energy distribution is found to be relatively cold, although we have not yet completely eliminated secondary rotational relaxation of the nascent products.

We have also set up a time-of-flight mass spectrometer to determine the internal state distribution of $N_2(X^1\Sigma_g^+)$ products from the uv photodissociation of HN_3, and eventually of N_3, by resonant-enhanced multiphoton ionization (REMPI) detection. We have obtained preliminary results for one-laser photodissociation/detection at the wavelength (283 nm) of the N_2 $a^1\Pi_g \leftarrow X^1\Sigma_g^+$ (1,0) band, which is used for the 2+2 REMPI process. The doubling crystal used in these experiments was damaged. This study is in abeyance until the repaired crystal is returned.

We are also interested in the electronic quenching of $NH(a^1\Delta)$ by N_2, in view of the calculations of Alexander and the study of infrared multiphoton dissociation of HN_3 at NIST, which suggest that there is a barrier in the spin-allowed decomposition channel [Eq. (1)]. This is also consistent with the recently measured small thermal rate constant for quenching of $NH(a^1\Delta)$ by N_2:

$$NH(a^1\Delta) + N_2 \rightarrow NH(X^3\Sigma^-) + N_2, \tag{7}$$

In our laboratory, we have set up a crossed beam apparatus for the measurement of state-to-state inelastic cross sections involving small free radicals. Here, rotationally cold free radicals are prepared in their lowest rotational states by photolysis of a suitable precursor diluted in a seed gas at the tip of the nozzle of a pulsed beam. The free radical beam is crossed with a pulsed target beam, and the rotational states of the former are interrogated by laser fluorescence detection. We have prepared rotationally cold beams of $NH(a^1\Delta)$ by photolysis of HN_3 seeded in N_2 or He. We have thus far measured pure rotationally inelastic cross sections for excitation out of the ground J=2 level of $NH(a^1\Delta)$ by various collision partners. We will be shortly turning to the study of the quenching process [Eq. (7)] in order to determine the internal state distribution of the quenched $NH(X^3\Sigma^-)$ products.

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The following persons have been involved in these projects:

Jing Chen, graduate student, The Johns Hopkins University.

Edwin Quiñones, postdoctoral fellow, The Johns Hopkins University.

Deborah G. Sauder, graduate student, The Johns Hopkins University.

Terrence Hemmer, graduate student, University of Maryland.

Hans-Joachim Werner, senior collaborator, Universität Bielefeld, W. Germany.

List of papers published and submitted since the inception of this contract:

1. M. H. Alexander, H.-J. Werner, and P. J. Dagdigian, "Energetics and Spin- and Λ-Doublet Selectivity in the Infrared Decomposition $HN_3(\tilde{X}^1A') \rightarrow N_2(X^1\Sigma_g^+) + NH(X^3\Sigma^-, a^1\Delta)$: Theory," J. Chem. Phys. **89**, 1388 (1988).

2. M. H. Alexander and P. J. Dagdigian, "Energetics and Spin Selectivity in the Infrared Multiphoton Decomposition Process $HN_3(\tilde{X}^1A') \rightarrow N_2(X^1\Sigma_g^+) + NH(X^3\Sigma^-, a^1\Delta)$," Amer. Inst. Phys. Conf. Proc., in press.